

Terazulene: A High-Performance n-Type Organic Field-Effect Transistor Based on Molecular Orbital Distribution Control

**azulene**

- large  $\mu$  (1.08D)
- blue color

< This Work >

• synthesis • UV-vis

• structure • n-type OFET

• Structure

• OFET characteristics

$T_{sub}$ (°C)	$\mu_{FEET}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
RT	$1.3 \times 10^{-2}$
60	0.10
100	0.29
140	$3.0 \times 10^{-2}$

• UV-vis

thin film

HOMO = -5.56 eV  
LUMO = -3.93 eV

• MO

LUMO

HOMO

2,6,12,12' hole

• Synthesis

pinB, CO<sub>2</sub>Me, NH<sub>2</sub>, HCl, toluene, 83%

pinB, CO<sub>2</sub>Me, Cl, Pd cat., 22%

Metal-Free Reductive Cleavage of C-N and S-N Bonds by Photoactivated Electron Transfer from a Neutral Organic Donor

Neutral organic super electron donor

1

Synthesis, OL, 2008, 6, 1227

NuH, NH<sub>3</sub> (l), 83%

$E_{1/2}$  (DMF) = -1.13 V vs Ag/Ag<sup>+</sup>/KCl (sat)

This study photoactivated

1. (6 eq), Ph, DMF, 72h, RT, 65%

2\* of ACIE, 2012, 51, 3673

Mechanism (DFT)

[Ph-N-Ts]<sup>•-</sup> → Ph-N + Ts<sup>•-</sup> (stable)

JACS, 2007, 129, 13368

2 (6 eq), DMF, 110°C, 74%

NE, dialkyl is no reaction.

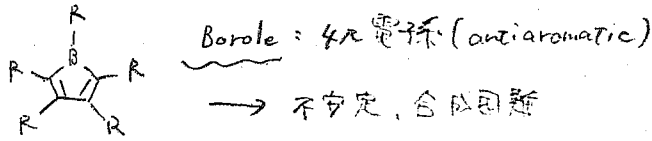
C<sub>12</sub>H<sub>25</sub>-N-Ts-Ph 1 (6 eq) → C<sub>12</sub>H<sub>25</sub>-N-H 80%

Ms LUMO fu, DMF

EWE<sub>1</sub> ⇒ CO<sup>+</sup>Bu

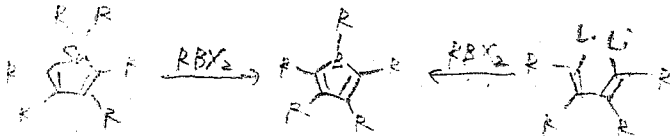
1 (6 eq), Ph, DMF, 83%

**Borole Formation by 1,1-Carbaboration**



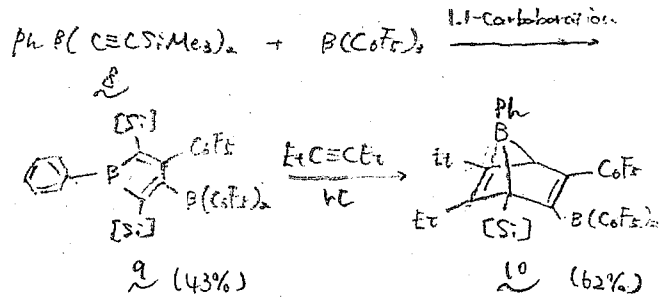
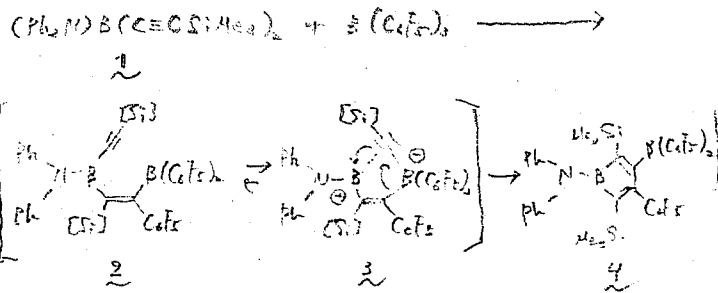
Previous synthetic method of borole

• Transmetalation



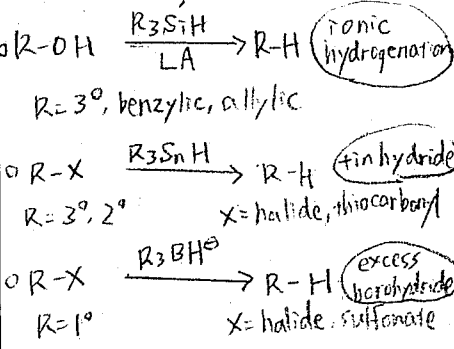
This work

• 1,1-carbaboration

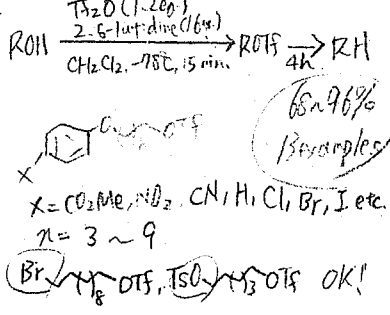


**Copper-Catalyzed Reduction of Alkyl Triflates and Iodides: An Efficient Method for the Deoxygenation of Primary and Secondary Alcohols**

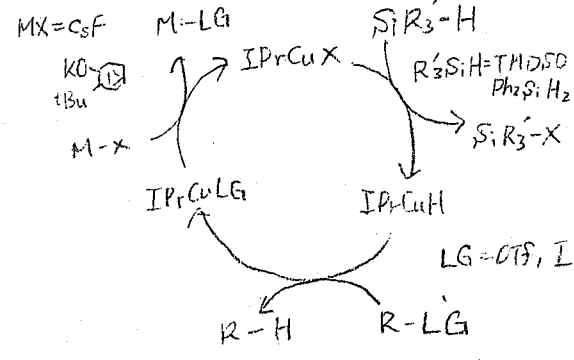
<Common Strategies>



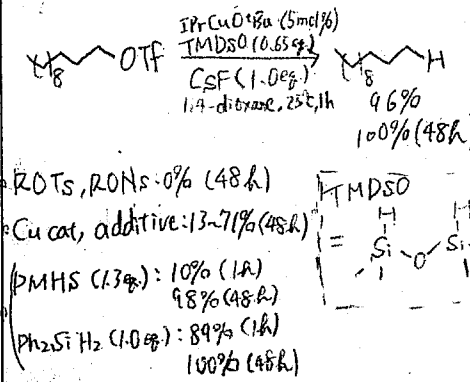
<Two-step deoxygenation>



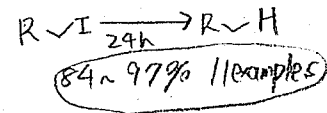
<Proposed catalytic cycle>



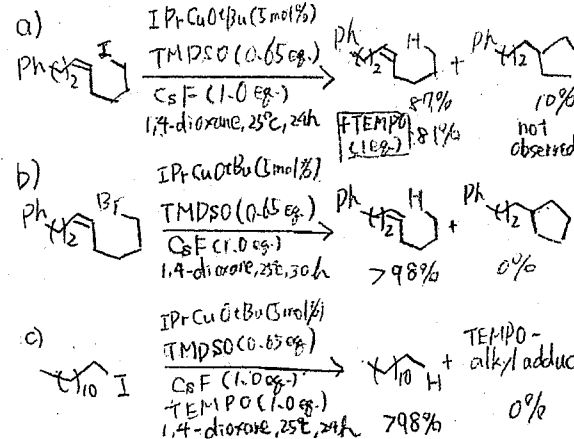
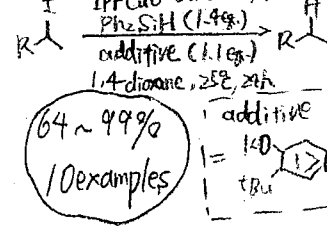
<Conditions>



<1° alkyl iodides>

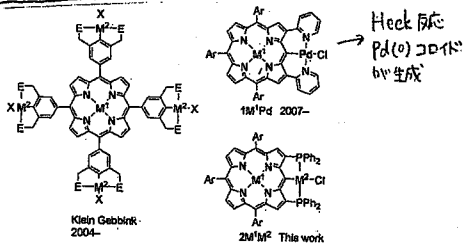


<2° alkyl iodides>



# Synthesis and Catalytic Activities of Porphyrin-Based PCP Pincer Complexes

## Introduction



Investigation the genuine catalytic activity

## Allylation ー 配位子の価数変化による

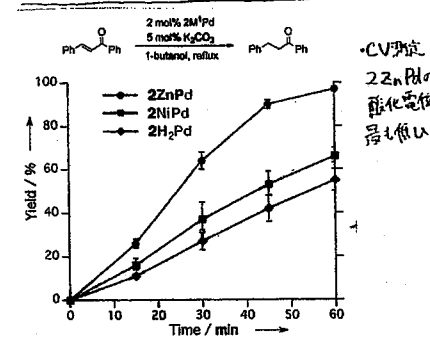
Table 1: Allylation of benzaldehyde with allylkin catalyzed by 2M<sup>M</sup>M<sup>2</sup>.

2M <sup>M</sup> M <sup>2</sup>	Yield [%] <sup>[a]</sup>	2M <sup>M</sup> M <sup>2</sup>	Yield [%] <sup>[a]</sup>	2M <sup>M</sup> M <sup>2</sup>	Yield [%] <sup>[a]</sup>
2NiNi	68	2ZnNi	90	2H <sub>2</sub> Ni	70
2NiPd	95	2ZnPd	97	2H <sub>2</sub> Pd	94
2NiPt	95	2ZnPt	88	2H <sub>2</sub> Pt	93

[a] Yields are those of isolated products.

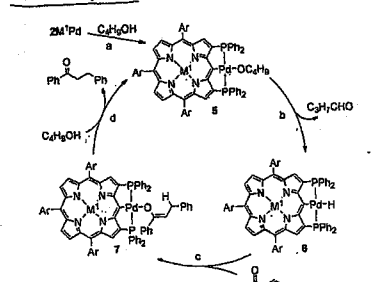
AgPF<sub>6</sub> ... M<sup>2</sup> 上の配位子のバリエーション

## 1,4-reduction of chalcone



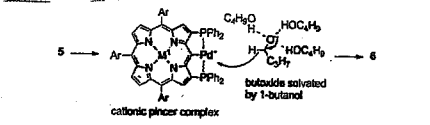
- 反応は inner metal に依存.
- Hg を加えると反応は進行する.
- PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(OAc)<sub>2</sub> では反応は進行しない.

## 触媒 cycle



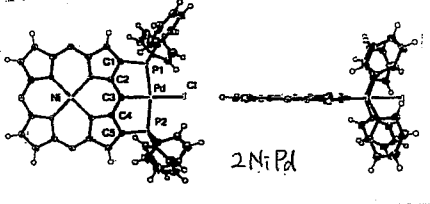
Scheme 2. Plausible mechanism of 1,4-reduction according to the report of Szabó et al.

## 触媒活性の探索

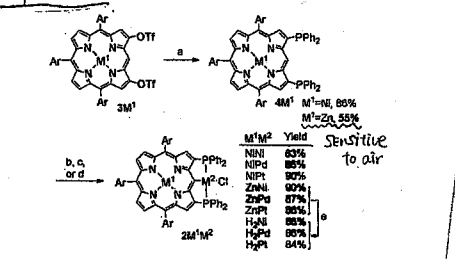


Scheme 3. Formation of palladium hydride through alcohol-promoted dissociative beta-hydride abstraction.

## 触媒の構造



## Synthesis

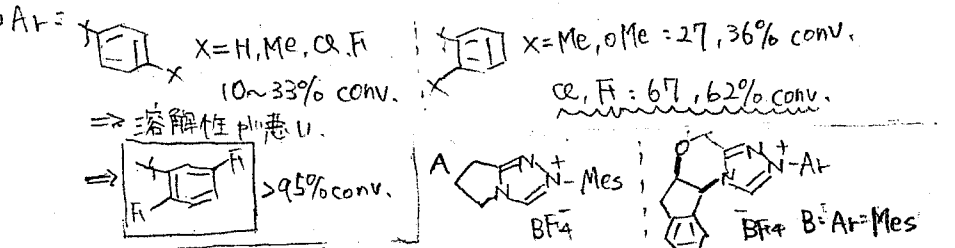
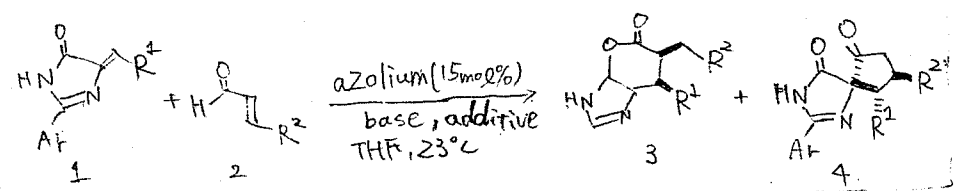


Scheme 1. Synthesis of porphyrin-based PCP pincer complexes. a) 5 equiv HPPPh<sub>2</sub>, 20 mol% Pd(OAc)<sub>2</sub>, 20 mol% dppb, 10 equiv NEt<sub>3</sub>, DMF, 90°C, 12 h; b) 1.1 equiv [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], 1.1 equiv NaOAc, toluene, 110°C, 24 h; c) 1.1 equiv [PdCl<sub>2</sub>(MeCN)<sub>2</sub>], 1.1 equiv NaOAc, toluene, 80°C, 3 h; d) 1.1 equiv K<sub>2</sub>PtCl<sub>6</sub>, 1.1 equiv NaOAc, toluene/DMF, 100°C, 10 h; e) TFA/CH<sub>2</sub>Cl<sub>2</sub>, 20°C, 10 min.

触媒の 2M<sup>M</sup>M<sup>2</sup> で幅広い吸収帯 (UV-Vis)  
⇒ 触媒活性の分子

# Enantioselective N-Heterocyclic Carbene Catalyzed Annulation Reactions with Imidazolidinones

## This Work

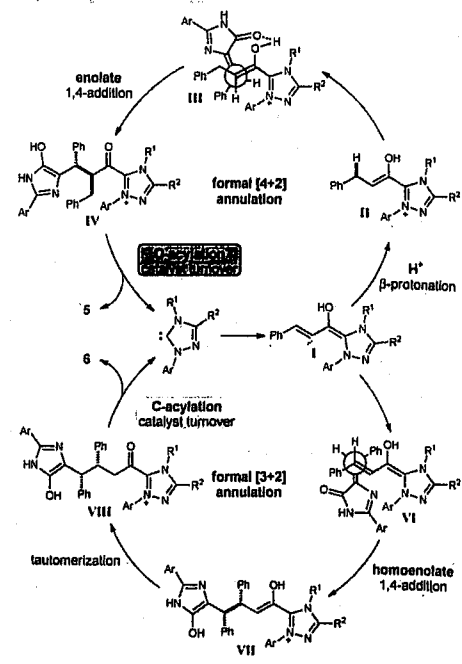


o azolium, base, additive.

No.	azolium	Base (eq.)	additive	Conv.	3/4	d.r. (3)	e.r.
1	A	Et <sub>3</sub> N (1.5)	—	85	55:45	10:1	—
2	B	Et <sub>3</sub> N (1.5)	—	84	63:37	10:1	95:5
3	C	Et <sub>3</sub> N (1.5)	—	75	66:34	10:1	98:2
4	C	Et <sub>3</sub> N (1.5)	AcOH (1.0 eq.)	81	82:18	11:1	98:2
5	C	nBu <sub>4</sub> NOAc (0.3)	—	94	82:18	6:1	98:2
6	C	nBu <sub>4</sub> NOAc (0.3)	AcOH (1.0 eq.)	96	91:9	6:1	98:2

Ar<sup>1</sup>, R<sup>2</sup>  
 R<sup>1</sup> = X = H, Cl, OMe, Me.  
 R<sup>2</sup> = X = H, OMe, Br, n-propyl, Me  
 46~90%

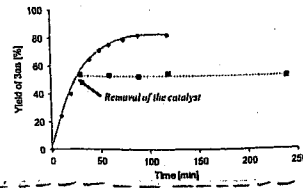
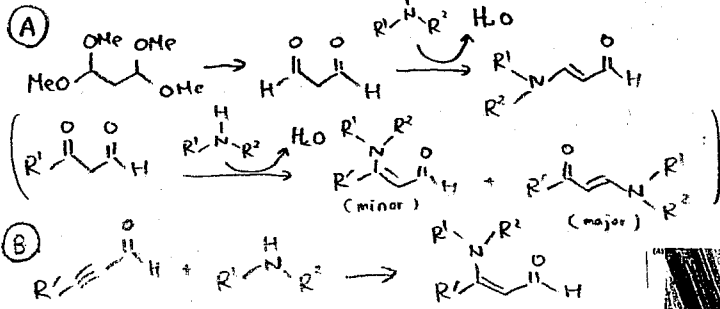
## Proposed Mechanism



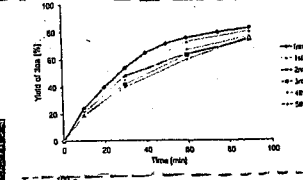
酸の存在 ⇒ β-protonation を促進!

Gold-Catalyzed Heterogeneous Aerobic Dehydrogenative Amination of  $\alpha$  &  $\beta$ -Unsaturated Aldehydes to Enaminal

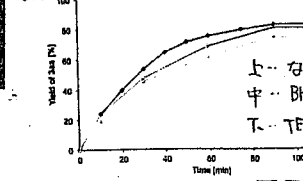
<Classical Procedures>



⇒ Au/OHS-2 catalyst  
EPRにて完全な  
T=100°Cに2時間

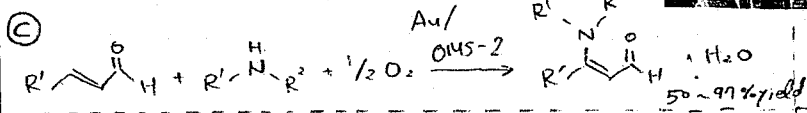


⇒ Au/OHS-2 catalyst  
は回収が3回まで可能  
少くとも5回は再使用  
可能



⇒ 反応は2時間以内  
に完了し、反応は5分  
以内

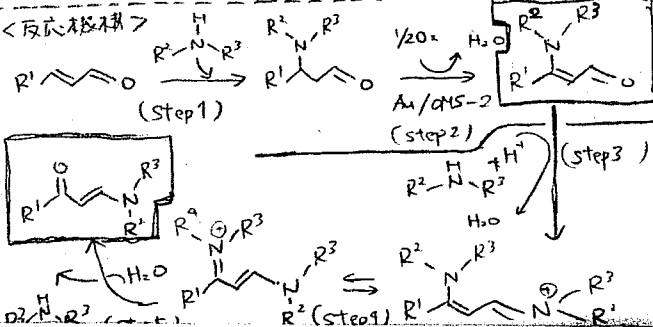
<This work>



<Optimization>

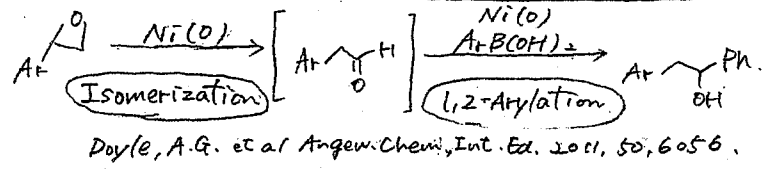
Catalyst	THF : H <sub>2</sub> O	2a (mmol)	Solvent
Pd/AR <sub>2</sub> O <sub>3</sub>	2 : 0	0.5	THF
Cu/AR <sub>2</sub> O <sub>3</sub>	1.95 : 0.05	1	CH <sub>2</sub> Cl <sub>2</sub>
Ru/AR <sub>2</sub> O <sub>3</sub>	1.9 : 0.1	1.5	DME
Au/AR <sub>2</sub> O <sub>3</sub>	1.8 : 0.2	2	Toluene

⇒ Au/OHS-2  
THF : water = 1.9 : 0.1  
2a = 1 mmol



Nickel-Catalyzed Regioselective Opening of Epoxides with Aryl Halides: Co-Catalysis Controls Regioselectivity

Previous Metal-catalyzed Coupling Reaction



Scope

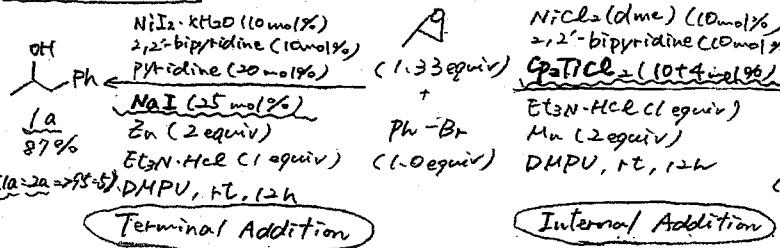
(TA) Ar-Br: EWG, EDG, 高橋  
⇒ 72 ~ 93%  
p-TSHNC<sub>6</sub>H<sub>4</sub> 84%  
p-HOC<sub>6</sub>H<sub>4</sub> 84%  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> 62%

(IA) Ar-Br: p-MeOC<sub>6</sub>H<sub>4</sub> 63% (2=1=4=1)  
p-MeO<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub> 62% (2=1=3.5=1)

R<sup>1</sup> = Alkyl: 76-82%  
R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub> 57%  
R<sup>1</sup> = BnO 69%  
R<sup>1</sup> = BocHN 60%  
R<sup>1</sup> = 65%

R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub> 57%  
R<sup>2</sup> = 6=1=1  
C<sub>6</sub>H<sub>5</sub> 41%  
R<sup>2</sup> = 2=1=99=1

This Work



Optimization

(TA) Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup> replace of NaI ⇒ 79% (1,2=95.5)

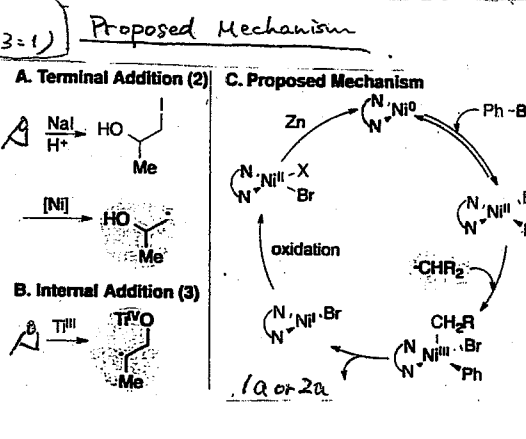
no NaI ⇒ 68% (1,2=95.5)

NaBr replace of NaI ⇒ 52% (1,2=95.5)

(IA) Cp<sub>2</sub>TiCl<sub>2</sub> (10 mol%), [NiI] (10 mol%), Cp<sub>2</sub>TiCl<sub>2</sub> (10 mol%), Et<sub>3</sub>N·HCl (1 equiv), Mn (2 equiv), DMPU, rt, 12h

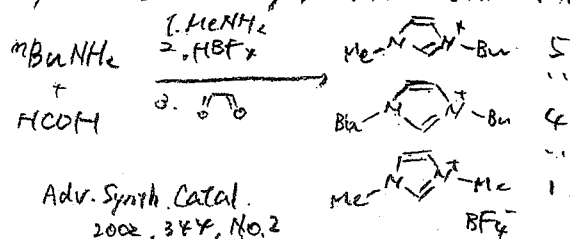
66% (trans/cis=26/74)

95% (trans/cis=99/1) (after 2h)



# Multi-component Synthesis of Unsymmetrical Unsaturated N-Heterocyclic Carbene Precursors and Their Related Transition-Metal Complex

## Synthesis of Unsymmetrical Unsaturated NHC Properties of complexes

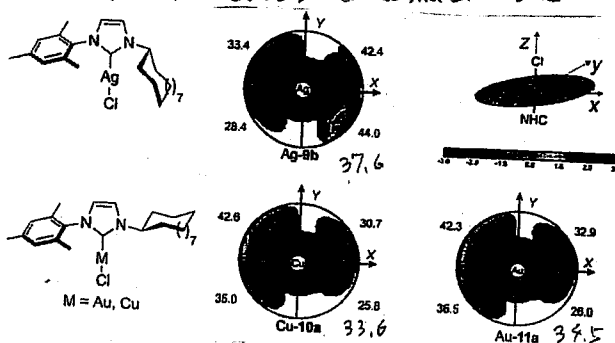


@ Tolman electronic parameter

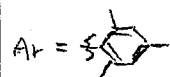
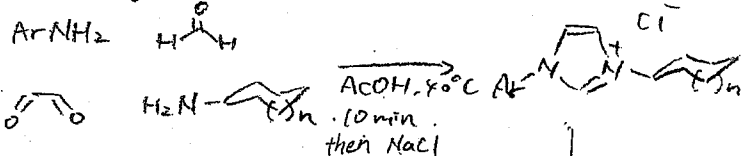
IMes-C5	2051.0 cm <sup>-1</sup>	IMes-C6	2050.5
IMes-C8	2050.6	IMes-C11	2050.5
IMes-C9	2050.7	(3,7) NHC 2050 cm <sup>-1</sup> 前掲	

値が大きいほど "electron poor"

@ Percent Buried Volume (% V<sub>bur</sub>) (IMes)AuCl ... 36.3 (IMes)AgCl ... 36.5



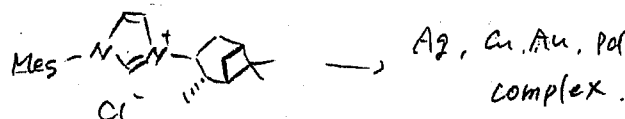
## This Work



n = 0, 3, 7  
 90-93% selectivity  
 55-80% yield  
 etc...

- (NHC)Rh(cod)Cl
- (NHC)AgCl
- (NHC)Ir(cod)Cl
- (NHC)CuCl
- (NHC)AuCl
- (NHC)Pd( $\pi$ -allyl)Cl

## Chiral unsymmetrical NHC



Paul Knochel

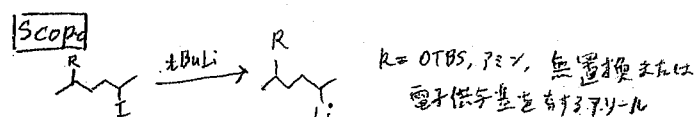
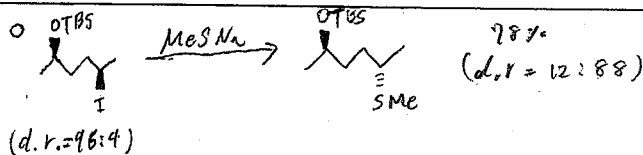
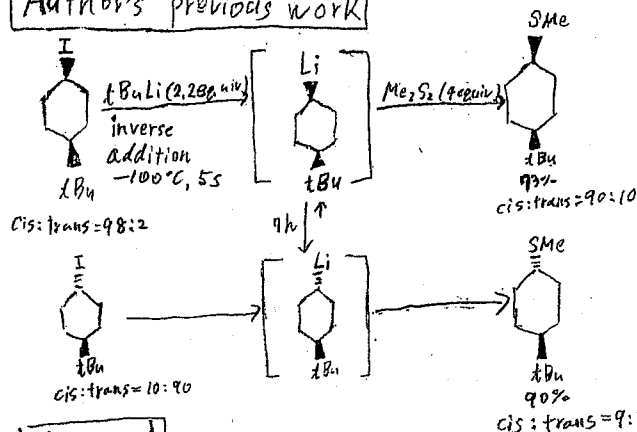
Ludwig-Maximilians-Universität München (Germany)

DOI: 10.1002/anie.201308679

M1 矢羽田

## Diastereoselective Synthesis of Open-Chain Secondary Alkylolithium Compounds and Trapping Reactions with Electrophiles

### Author's previous work

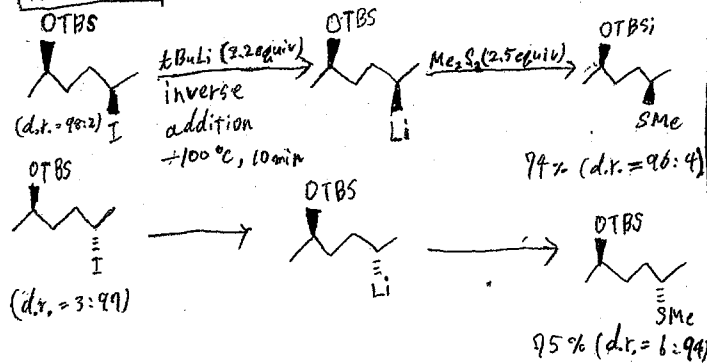


E <sup>+</sup>	X
S <sub>2</sub> K <sub>2</sub>	-SR (R = 2-pyridyl, 2-thienyl)
PhSOCl	-Cl (R = 2-pyridyl)
DMF	-CHO
CO <sub>2</sub>	-CO <sub>2</sub> H (R = 2-pyridyl)

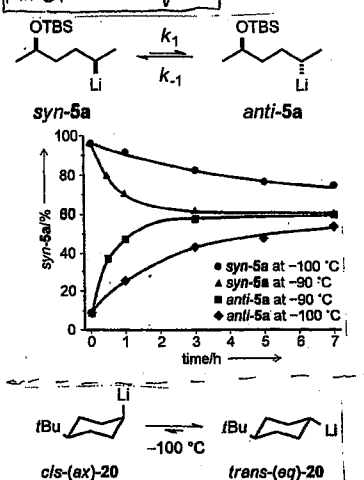
yield 58-81%

syn: d.r. = 91:9 ~ 96:4  
anti: d.r. = 9:91 ~ 4:96

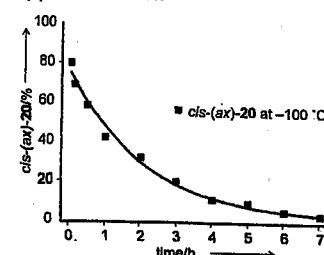
### This work



### Kinetic investigation

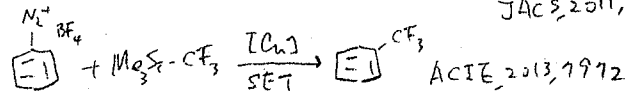
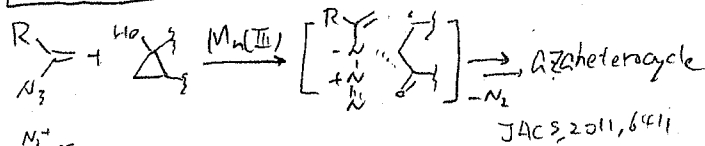


### a) previous work [8a]

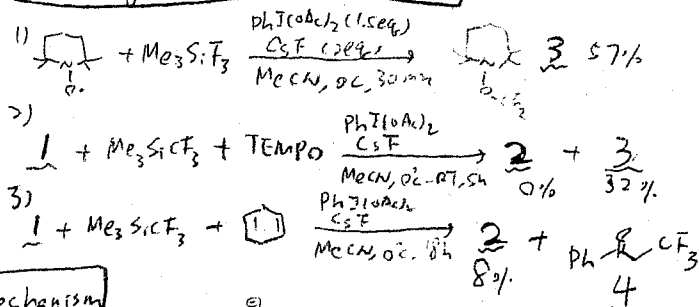


PhI(OAc)<sub>2</sub>-Mediated Radical Trifluoromethylation of Vinyl Azides with Me<sub>3</sub>SiCF<sub>3</sub>

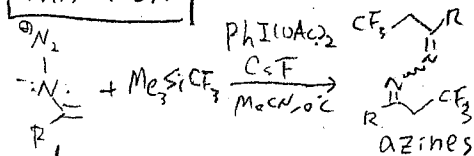
Previous Work



Investigation of Mechanism



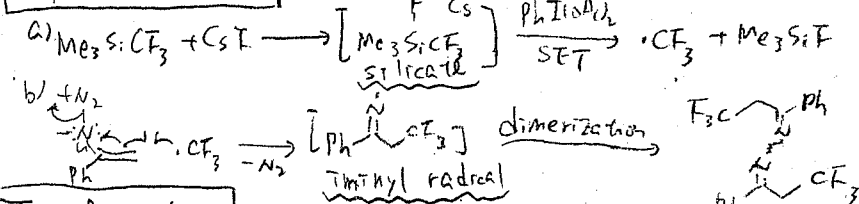
This Work



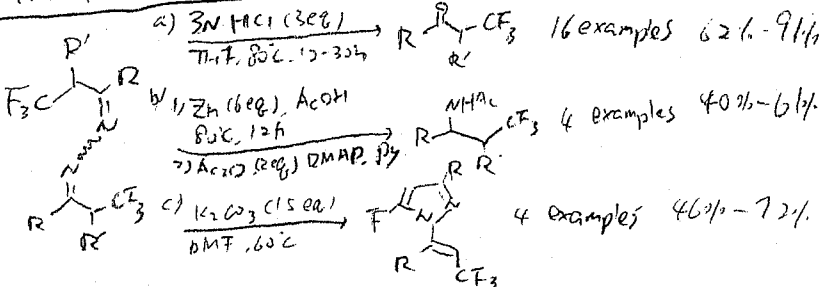
Optimization

F <sup>+</sup> source (eq.)	Conditions	Yield (%)
CsF (0.5)	0°C, 3h	72
CsF (1)	0°C, 1h	14
CsF (1.5)	0°C, 30min	96
KF (2)	0°C-RT, 24h	70
—	0°C-RT, 24h	0

Proposed Mechanism



Transformation

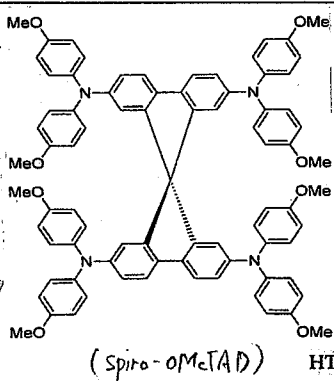


Efficient Inorganic-Organic Hybrid Perovskite Solar Cells Based on Pyrene Arylamine Derivatives as Hole-Transporting Materials

〈太陽電池〉

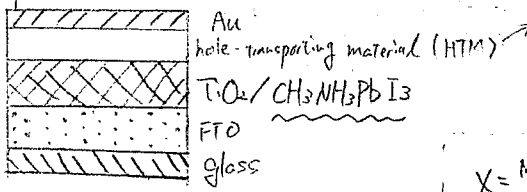
シリコン →

- ・色素増感太陽電池
- ・有機太陽電池
- ・無機-有機ハイブリッド太陽電池



	λ <sub>max</sub> (nm) <sup>a</sup>	E <sub>opt</sub> (eV) <sup>b</sup>	E <sub>pc</sub> (mV) <sup>c</sup>	E <sub>p</sub> (mV) <sup>c</sup>	E <sub>onset</sub> (mV) <sup>c</sup>	E <sub>onset</sub> (eV) <sup>c</sup>	E <sub>LUMO</sub> (eV)
Py-A	420	2.63	292	166	229	-5.41	-2.78
Py-B	470	2.43	133	-1	66	-5.25	-2.82
Py-C	492	2.36	-28	-119	-74	-5.11	-2.74
Spiro-OMeTAD	388	2.95	83	-9	37	-5.22	-2.27

previous work



交換効率 (η) 15%  
 (Nature, 2013, 499, 316.)

This work

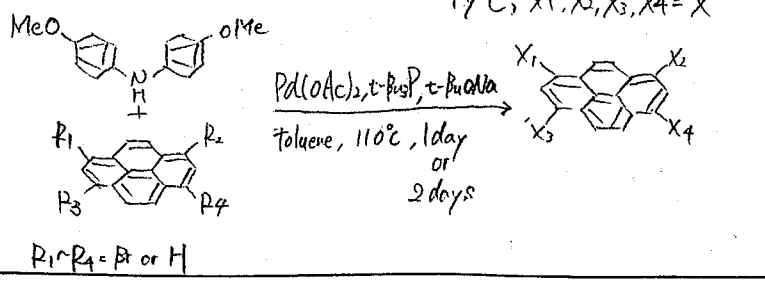
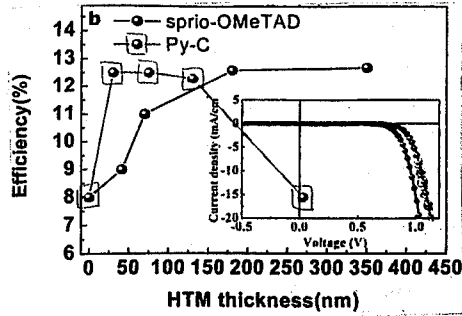


Table 1.

Table 2. ↓

HTM	J <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	η (%)	R <sub>s</sub> (Ω)
without	17.7	0.80	56.5	8.0	65.6
Py-A	10.8	0.89	34.6	3.3	402.2
Py-B	20.4	0.95	63.7	12.3	64.3
Py-C	20.2	0.89	69.4	12.4	51.6
Sp-A	20.2	0.83	61.8	10.3	64.6
Sp-B	21.0	1.01	59.5	12.7	85.9



← the efficiency dependence on the overlayer thickness